STRATEGIES USING VEGETABLE OIL FOR ENHANCED BIOREMEDIATION OF CHLORINATED SOLVENTS

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Introduction

- Many organic substrates have been used to stimulate reductive dechlorination of chlorinated solvents in groundwater
- Vegetable oil (VegOil) has been selected for study by the Air Force as a low-cost alternative substrate
- Strategies for using vegetable oils have been developed (revised protocol pending)
- The effectiveness and cost of two VegOil applications is presented for Site SS015 at Travis AFB, CA and the Hangar K Site at Cape Canaveral Air Station, FL

Vegetable Oil Injection for Enhanced Bioremediation

- Involves injection of food-grade vegetable oil which is only slightly soluble in groundwater (<1,000 mg/L)
- Costs $0.25 to $0.50/pound delivered
- Allows a one-time injection scenario – big benefit/cost savings
- Soybean oil is being tested by AFCEE at seven sites in CA (2), FL, OK, MO, OH, DE
- Additional tests are planned in 2003 in OK, HI, TX, and WA

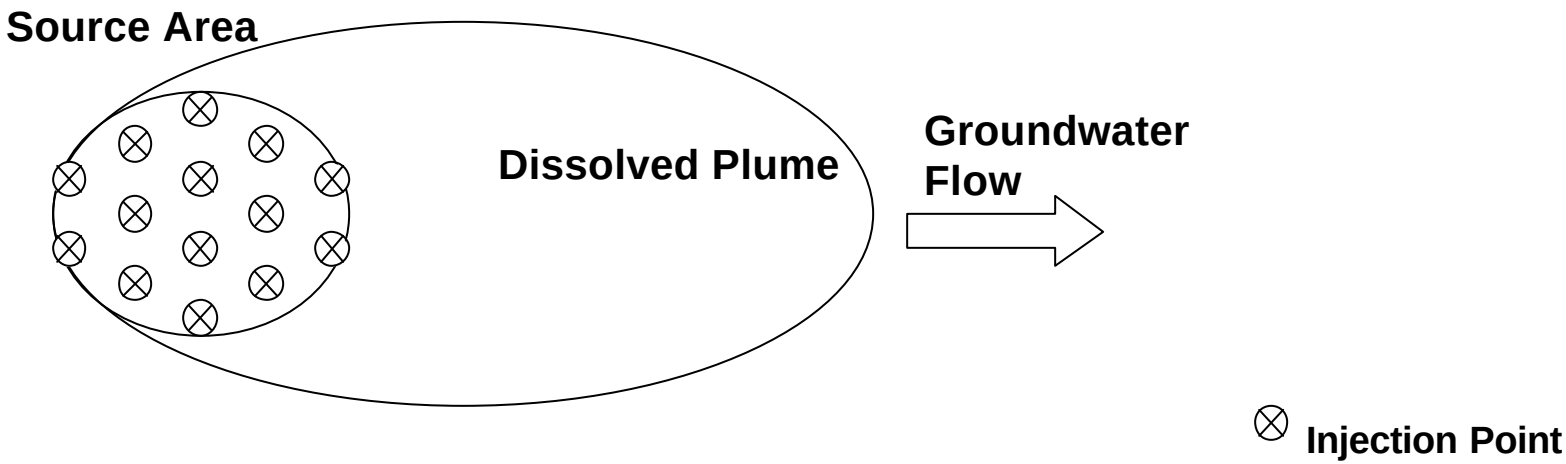
Vegetable Oil Injection for Enhanced Bioremediation

Primary objective is to reduce source mass and/or prevent plume migration by stimulating reductive dechlorination of chlorinated solvents

Two strategies are commonly applied:

- **Reduce or contain source mass in a known source area or a plume "hotspot" (grid configuration)**
- **Prevent plume migration through containment/interception (permeable biobarrier configuration)**

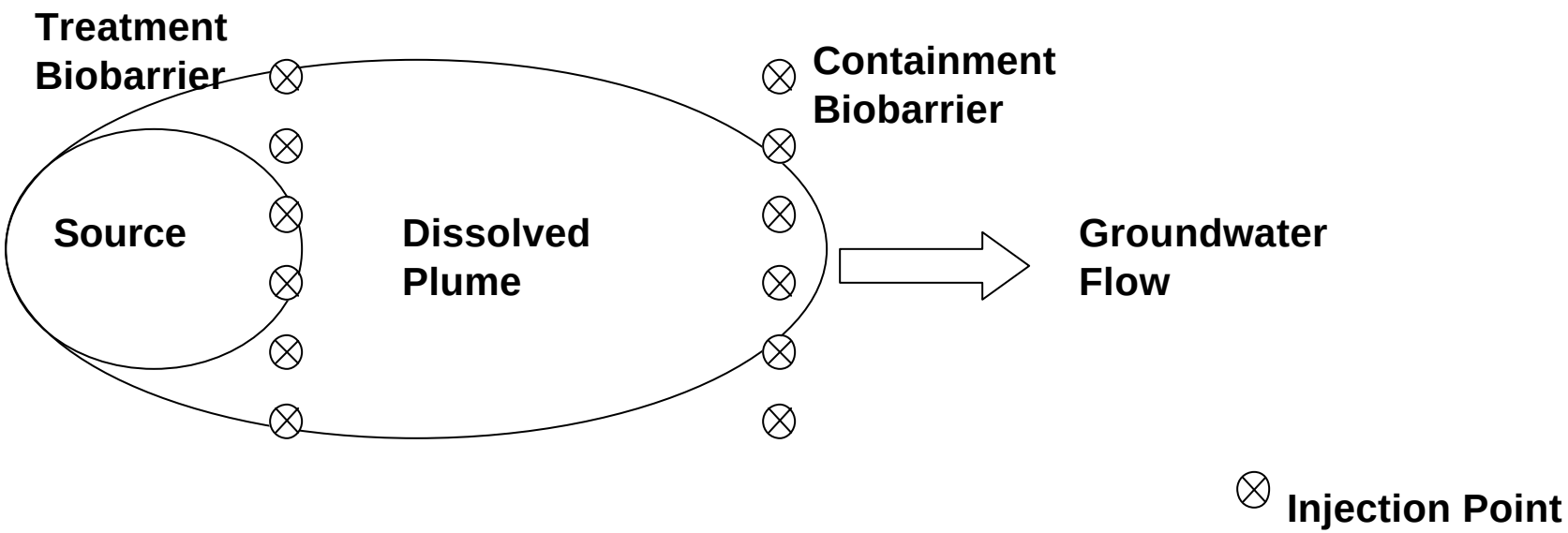
Source Area Configuration



Source Area Configuration

- Sorbed mass is “stripped” from the aquifer matrix by the surfactant properties of the oil
- Contaminant mass partitions into the vegetable oil (sequestered/contained)
- Mass is destroyed by degradation processes
- Dissolution from DNAPL or sorbed mass is enhanced by increased concentration gradients
- Partitioned contaminant mass is released into the reaction zone as the oil degrades
- Relative permeability (i.e., hydraulic conductivity) may be intentionally lowered to reduce mass flux from the source area (containment)

Biobarrier Configuration



Biobarrier Configuration

- Biobarrier intercepts groundwater flow and contaminant mass flux
- Contaminant mass partitions into the vegetable oil (short term reduction in contaminant concentrations)
- Mass is destroyed by degradation processes (long term reduction in contaminant concentration and mass)
- But, maintaining hydraulic conductivity in the biobarrier is paramount (use of emulsions and lower residual oil saturations)
- Mobile micro-emulsions and lower residual saturations will reduce longevity of biobarrier

Substrate Distribution

- Design of oil-in-water emulsions with very fine droplet size to increase radius of influence
- Better distribution and greater surface area of oil in an emulsion may stimulate quicker degradation
- Use of direct-push injection to increase injection grid density or to lower cost
- Advection/diffusion of dissolved substrate (mostly highly soluble metabolic acids from degradation of the oil)

Partitioning/Surfactant Effects

- **Partitioning of contaminant mass into vegetable oil *temporarily* contains the contaminants until the oil begins to degrade**
- **Mass partitions back into an active reaction zone as oil degrades or as dissolved concentrations decrease**
- **Surfactant properties increase the amount of sorbed or residual mass that is bioavailable for degradation**

Effects on Hydraulic Conductivity

- **Residual oil concentrations lower hydraulic conductivity**
- **Degradation of vegetable oil over time may decrease residual saturation, but increase biomass**
- **Use of dilute oil-in-water micro-emulsions may maintain hydraulic conductivity, but are more mobile and may have less longevity**
- **Reducing hydraulic conductivity may be beneficial as a source containment measure, but is not desirable for permeable biobarriers**

Substrate Dissolution/Degradation

- **Complex substrates such as molasses and vegetable oil are first degraded producing metabolic acids (propionic, butyric, acetic), which in turn are fermented to produce hydrogen**
- **Molecular hydrogen is the most effective electron donor for reductive dechlorination**
- **Metabolic acids produced by oil degradation are highly soluble and they disperse by advection and diffusion. Thus, they behave in a manner similar to other common substrate types**

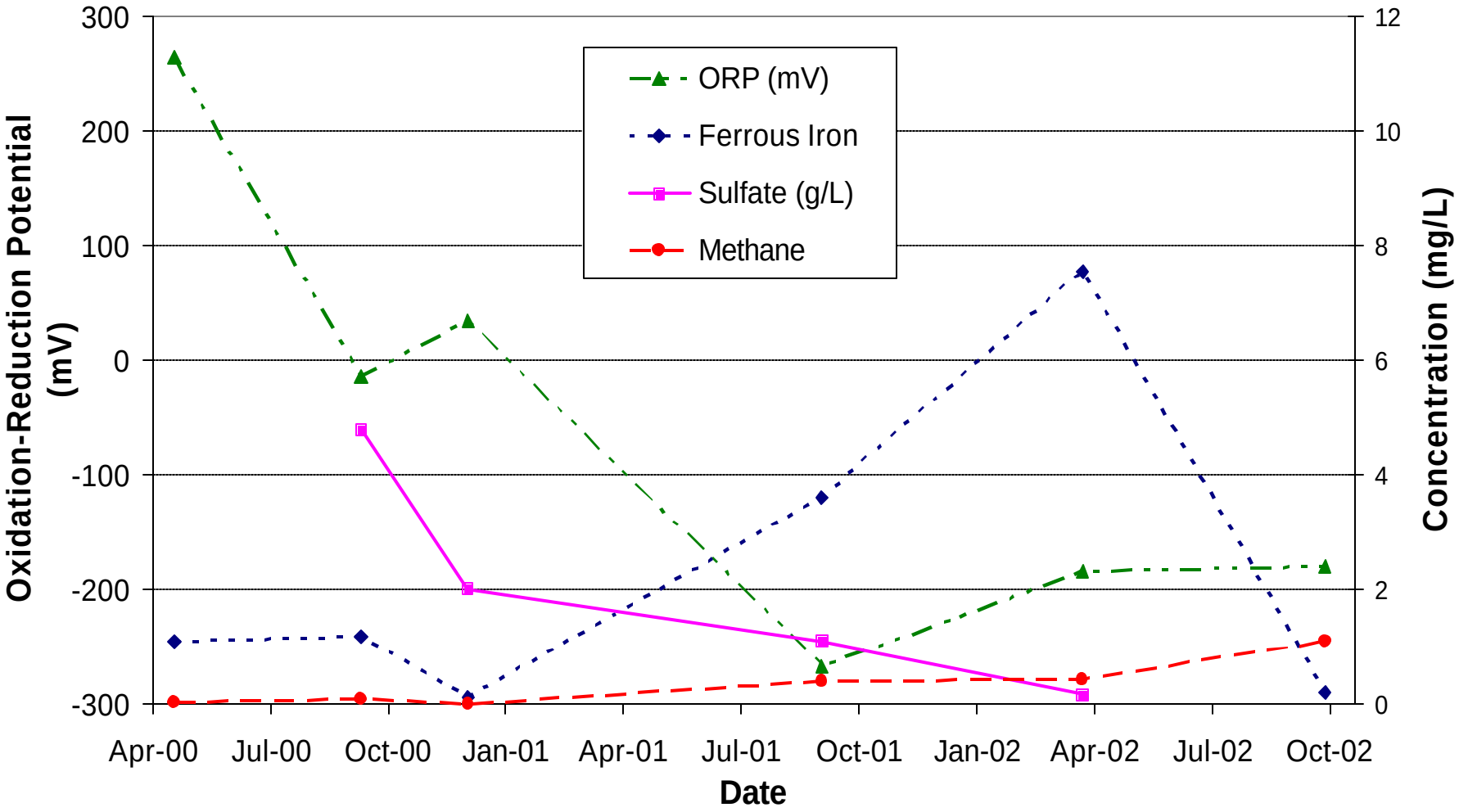
VegOil Injection at Travis AFB

VegOil Application at SS015

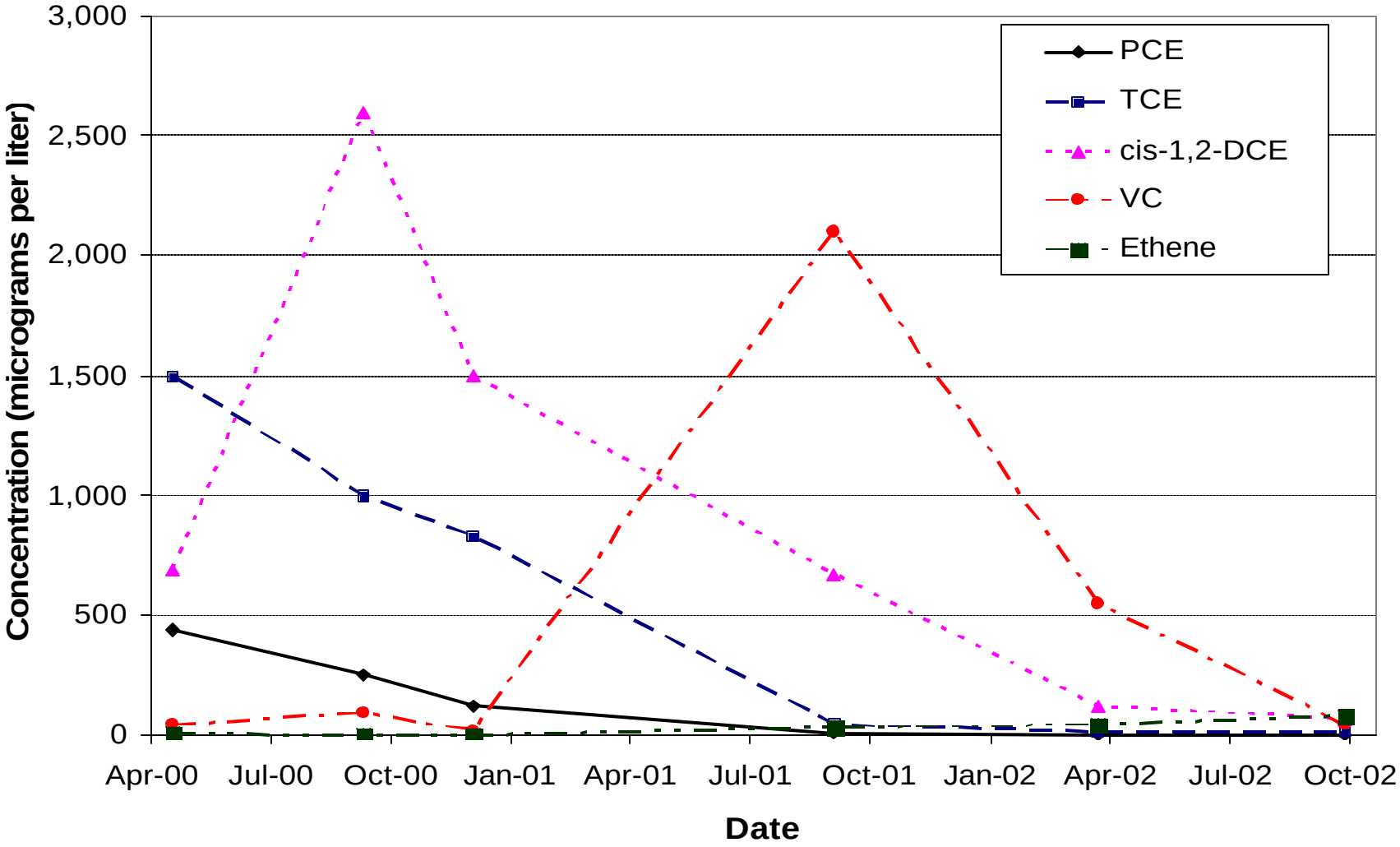
STRATEGY: Source reduction in a low permeability, high sulfate aquifer

- **Initial contaminant concentrations as high as 4 mg/L TCE, 13 mg/L *cis*-1,2-DCE, and 17 mg/L VC**
- **Initial sulfate concentrations as high as 5,400 mg/L**
- **62 gallons of VegOil injected in June 2000 (pilot-scale)**
- **150 gallons of VegOil injected as an emulsion in December 2000 (expanded-scale)**
- **Additional 250 gallons of VegOil as an emulsion in April 2002 (full-scale)**
- **At some locations the emulsion was injected at sufficient pressure to fracture the formation and improve substrate distribution**

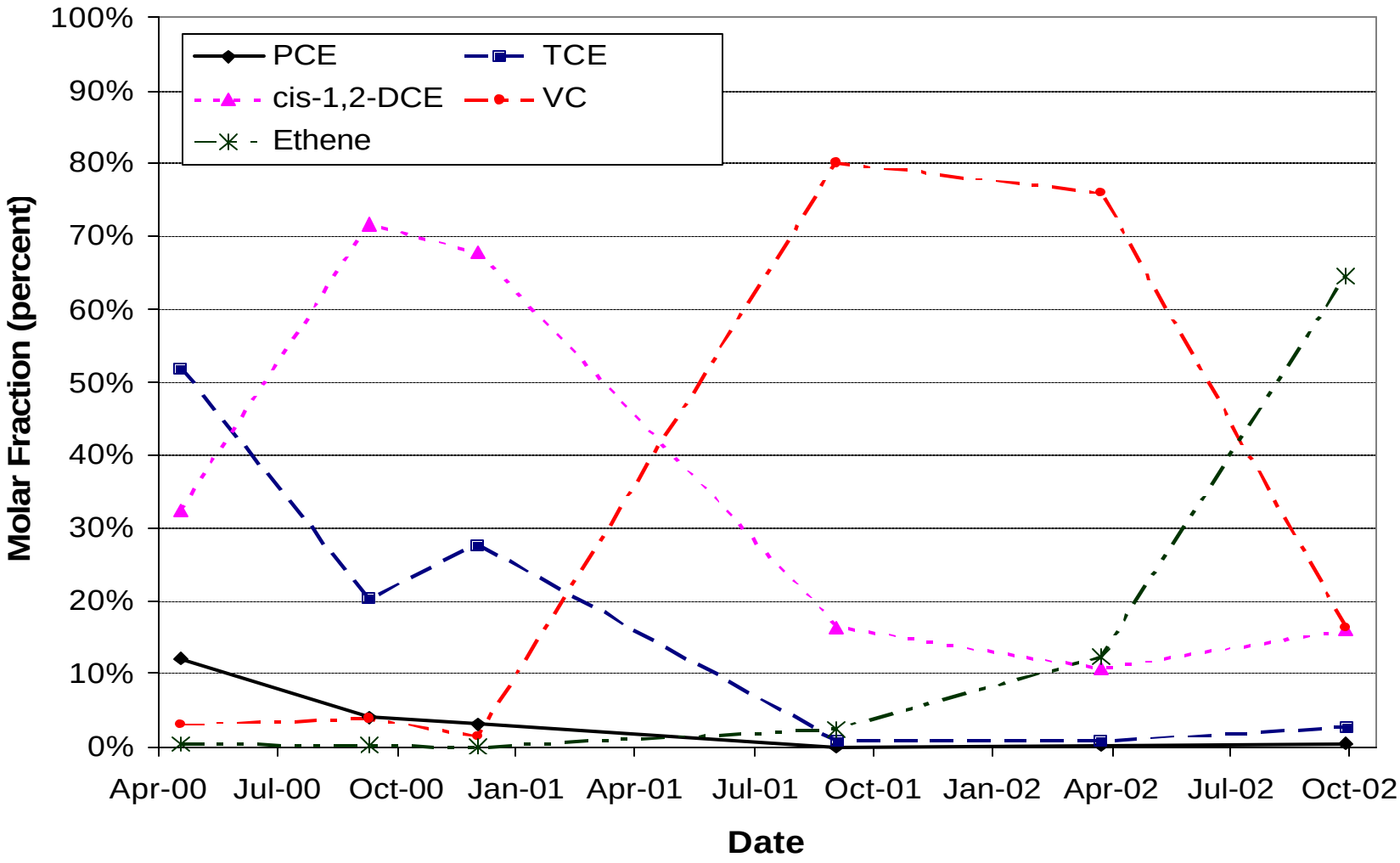
Geochemistry at Well PES-MW4



Changes in Contaminant Concentrations at Well PES-MW4



Changes in Molar Fraction at Well PES-MW4



Travis VegOil Summary

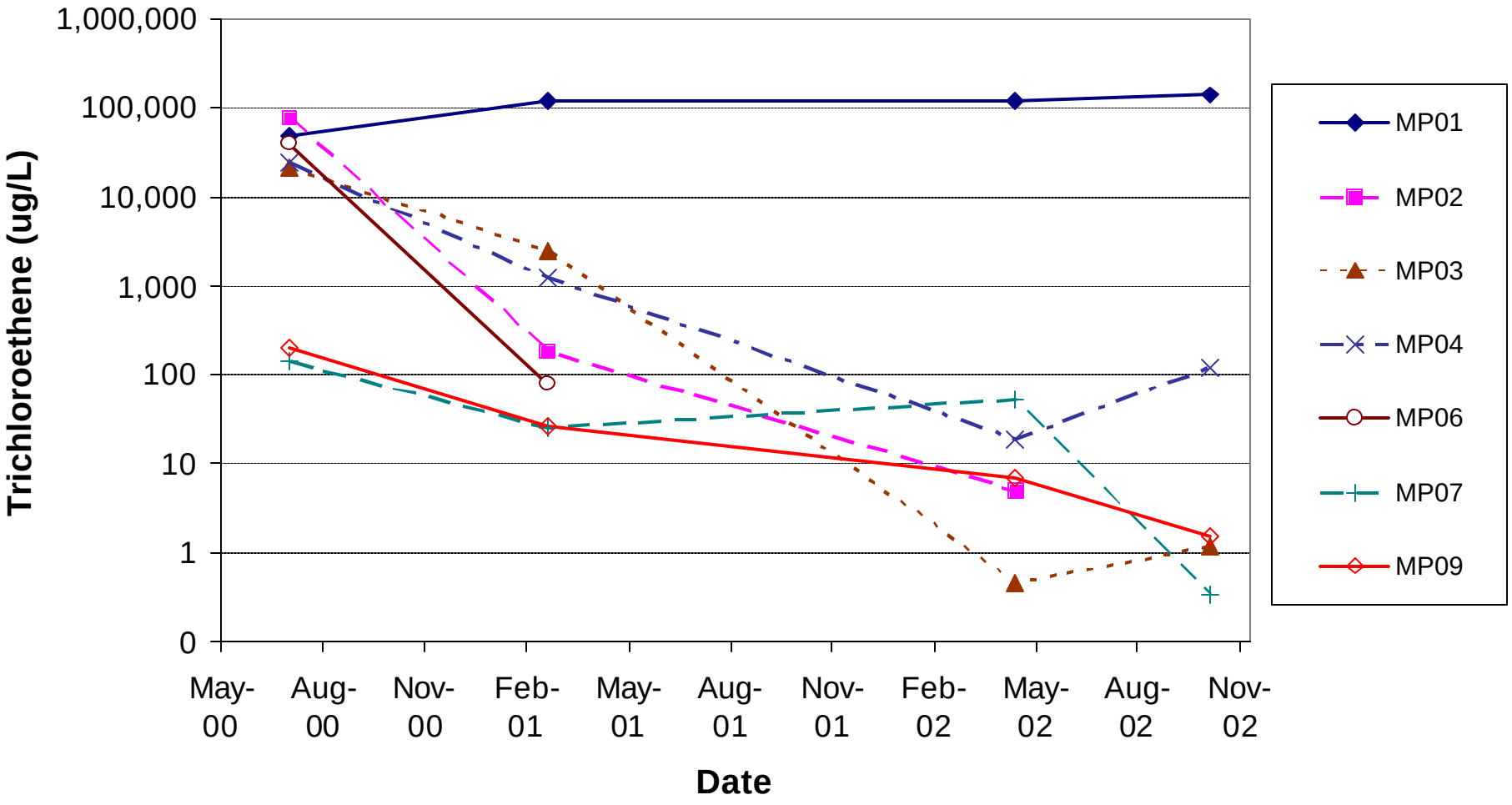
- Reductive dechlorination was observed at all locations, even with sulfate at 1,500 to 3,000 mg/L
- Complete reduction of PCE and TCE to ethene and ethane is being observed with an average of 96% reduction in TCE
- Some temporal accumulation of VC was observed, but overall VC has decreased from a maximum of 17 mg/L pre-injection to a maximum of 0.5 mg/l in October 2002
- Methane remains relatively low (< 2 mg/L), indicating good utilization of substrate for dechlorination

VegOil Application at Cape Canaveral Hanger K Site, FL

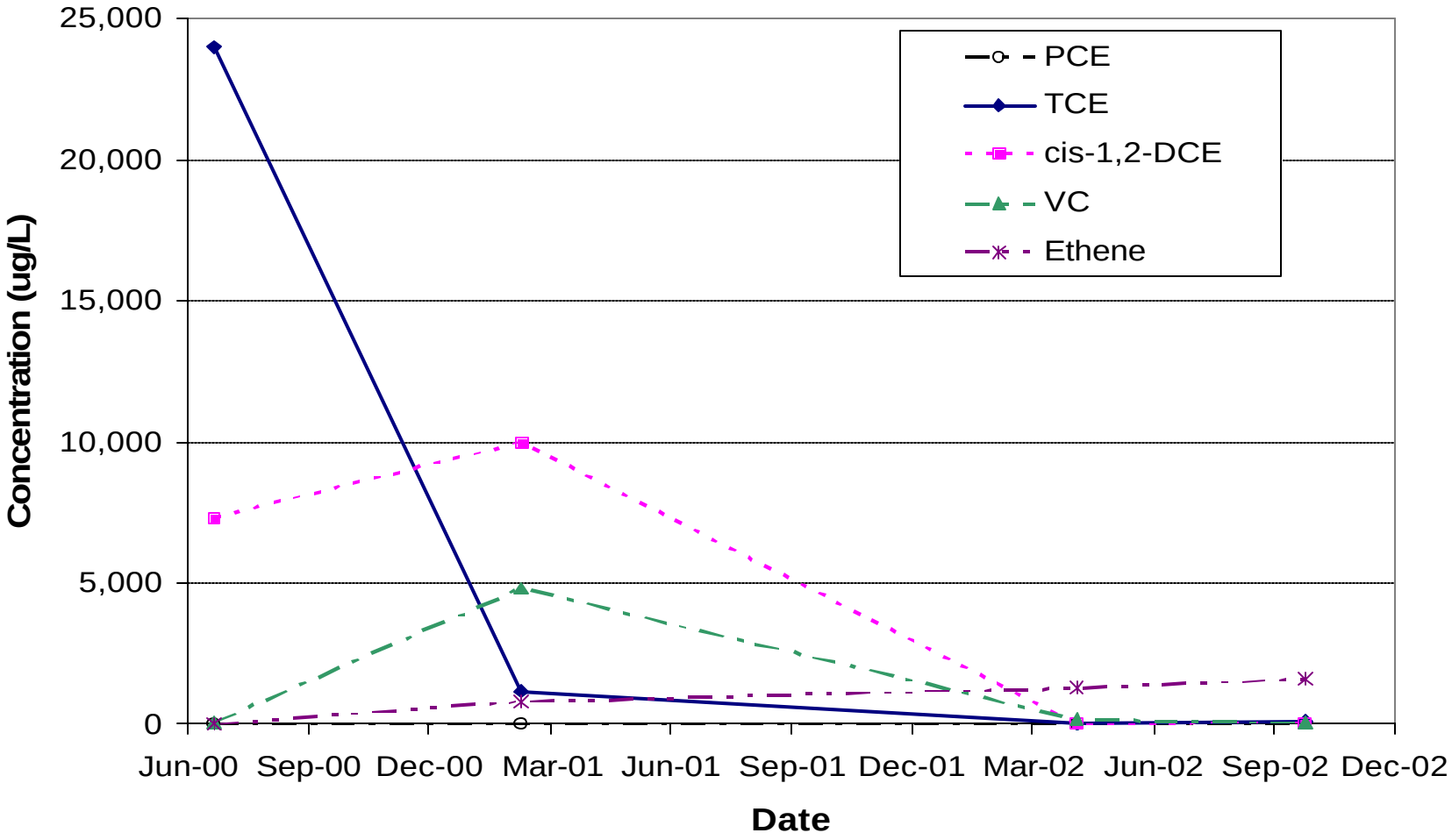
STRATEGY: Source reduction in presence of DNAPL in a high permeability aquifer

- **Initial TCE concentrations as high as 100 mg/L, indicating presence of DNAPL**
- **1,815 gallons of VegOil injected straight in August 2000 followed by 6,600 gallons of native groundwater as a water push to improve the effective radius of influence**
- **Treatment area of 5,000 square feet and aquifer volume of 150,000 gallons**
- **The coarse grained nature of aquifer allowed the VegOil and water push to be injected at relatively low pressure and high flow rate**

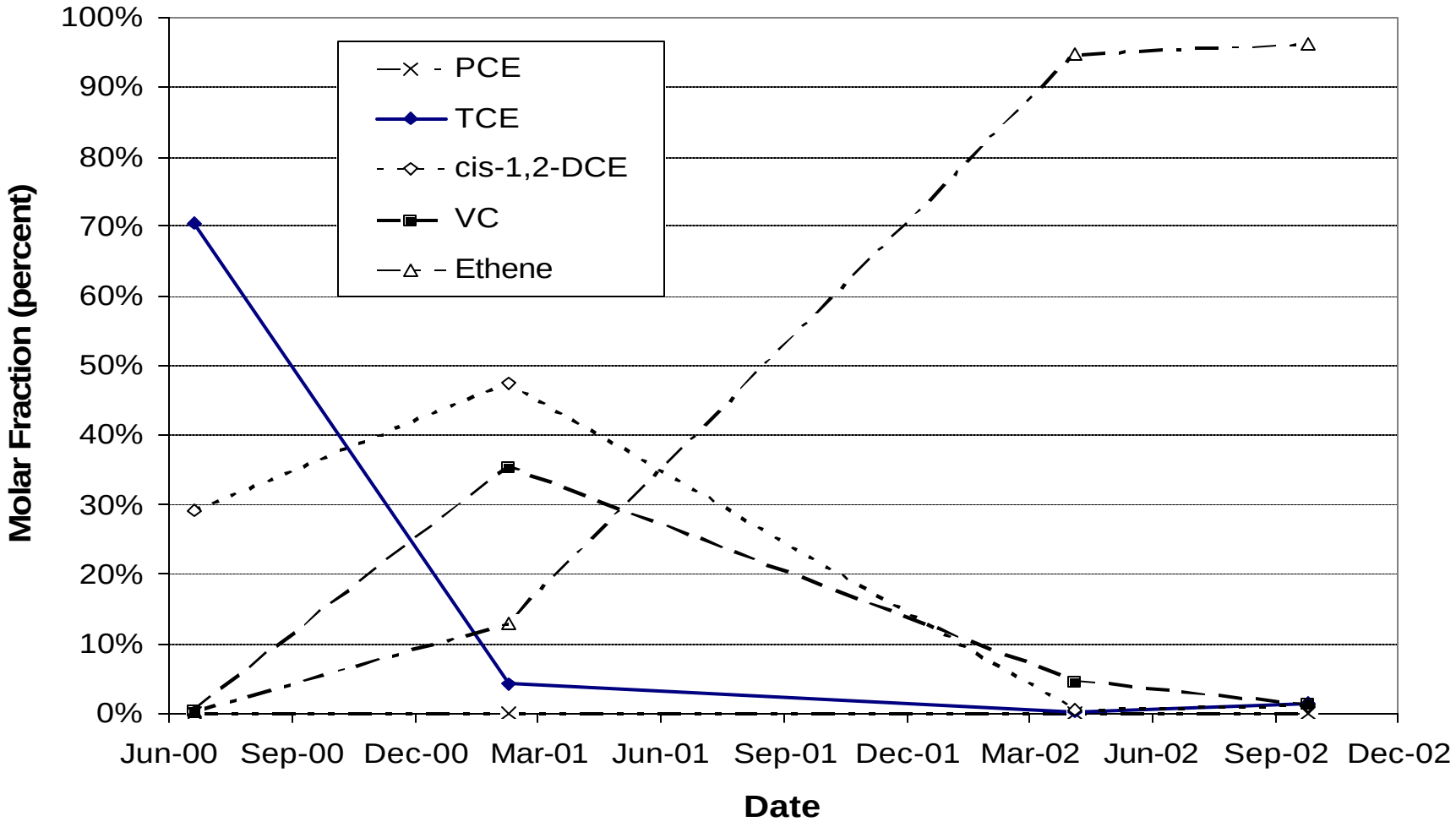
TCE over Time at Cape Canaveral Hangar K Site



Changes in Concentration at Well HGRK-MP04



Changes in Molar Fraction at Well HGRK-MP04



Cape Canaveral Hanger K Results

- Up to four orders of magnitude reduction of TCE, with initial TCE concentrations as high as 100 mg/L
- PCE and TCE reduced to less than MCLs at 8 of 12 locations monitored in October 2002
- VC initially accumulated due to kinetic disparity, but has been steadily decreasing since April 2002 (VC is below MCL at 3 locations)
- Conversion to ethene and ethane is being observed at all monitoring wells

VegOil Implementation Costs

	Travis	Cape Canaveral
VegOil Implementation Costs – Phase II		
Work Plan Preparation	$12,000	$11,000
Installation / Injection	$31,100	$38,300
Substrate (VegOil)	$1,100 (3,200 lb)	$5,700 (13,200 lb)
Reporting	$12,000	$12,000
Total	$56,200	$67,000
Annual Performance Monitoring Costs (2 Events)		
Sampling and Analysis	$32,000	$32,000
Reporting and Administration	$12,000	$12,000
Total	$44,000	$44,000

Conclusions

- **Despite differences in lithology and geochemistry, the VegOil option has successfully reduced chlorinated ethene mass by reductive dechlorination to the end products of ethene and ethane at both sites**
- **Accelerated chlorinated ethene mass depletion was observed sooner, and has proceeded at a faster rate, at the Cape Canaveral Site**
- **Implementation and performance monitoring costs are nearly identical for both sites**
- **Process monitoring is a significant cost relative to substrate emplacement**